

# Report 40850R24 Revision 1

## Final Technical Report

### Demonstration of Black Liquor Gasification at Big Island

Reporting Period Start Date: **February 15, 2001**

Reporting Period End Date: **November 30, 2006**

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Reporting Date: **January 12, 2007**    **Revision 1 March 22, 2007**

DOE supplied modifications: **March 21, 2007** (Added Appendix 8)

DOE Award Number: **DE-FC22-01NT40850**

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Throughout this project, Georgia-Pacific LLC has appreciated the opportunity to work on this new technology project and undertaking with all parties involved in an effort to promote the advancement of the science of biomass gasification. In no way should any statement of GP be construed as any criticism of any company, contractor, researcher or governmental agency, as all parties have attempted in good faith to expand the scientific understanding in this area through trial and experimentation. Success and failure is part of the process of pursuing new science and technology. Our sole intent also is to promote good science through describing the facts in this project, and we hope that others will be able to carry on further experimentation in the scientific development of black liquor gasification.

## **ABSTRACT**

This Final Technical Report provides an account of the project for the demonstration of Black Liquor Gasification at Georgia-Pacific LLC's Big Island, VA facility. This report covers the period from May 5, 2000 through November 30, 2006.

## TABLE OF CONTENTS

|   |    |
|---|----|
| Title Page .....  | 1  |
| Disclaimer .....  | 2  |
| Abstract .....  | 3  |
| Table of Contents .....   | 4  |
| Abbreviations and Acronyms .....  | 5  |
| Project Description .....   | 7  |
| Summary .....   | 8  |
| Discussion and Results .....  | 11 |
| Experimental .....  | 15 |
| Conclusion .....  | 17 |
| Patents and Publications .....  | 17 |
| Acknowledgements .....  | 17 |
| Appendix 1 – Performance Comparison .....   | 18 |
| Appendix 2 – Simplified Process Flow Diagram .....  | 19 |
| Appendix 3 – Simplified Process Balance .....   | 20 |
| Appendix 4 – Quarterly Reports .....  | 21 |
| Appendix 5 – Pulse Heater Picture .....   | 34 |
| Appendix 6 – Fluidizing Grid Diagram .....  | 35 |
| Appendix 7 – Project Cost Summary .....   | 36 |
| Appendix 8 – Summary of Steam Reformer Operational, Maintenance, Experience and<br>Achievements at Norampac ..... | 38 |

## ABBREVIATIONS AND ACRONYMS

|              |   |
|--------------|---|
| BL           | Black Liquor - the spent pulping liquor from the digesters used as a fuel, in this case non-sulfur sodium carbonate   |
| BYU          | Brigham Young University - Provo, UT  |
| DOE          | Department of Energy - in this case the Energy Efficiency and Renewable Energy Office of Biomass Programs   |
| dummy tubes  | Inactive pulse heater tubes fitted with internal thermocouples. These tubes were designed to provide an indication of the temperature of the bed within the pulse heater bundle and an indication of possible bed side plugging.                      |
| EPA          | Environmental Protection Agency, in this case Region III  |
| F            | Temperature in Degrees Fahrenheit   |
| Fluor        | Fluor Corporation - Greenville, SC and Aliso Viejo, CA  |
| Georgia Tech | Georgia Institute of Technology - Atlanta, GA   |
| GL           | Green Liquor - pulping liquor sent to the digesters, in this case non-sulfur sodium carbonate   |
| GP           | Georgia-Pacific LLC - Atlanta, GA and GP Big Island LLC - Big Island, VA  |
| HRSG         | Heat Recovery Steam Generator   |
| IPST         | Institute of Paper Science and Technology - Atlanta, GA   |
| KMPS         | Koch Modular Process Systems - Paramus, NJ  |
| LBNL         | Lawrence Berkeley National Laboratory of the Department of Energy - Berkeley, CA  |
| MACT II      | Maximum Achievable Control Technology - a portion of the federal Clean Air Act  |
| mmbtu/hr     | Million British Thermal Units per hour  |
| MTCI         | Manufacturing and Technology Conversion International - Baltimore, MD<br>Technology Developer, Patent Holder & Licensor of the PulseEnhanced™ steam reforming technology  |
| NDE          | Non-Destructive Examination   |
| NETL         | National Energy Technology Laboratory of the Department of Energy - Morgantown, WV and Pittsburgh, PA   |
| OEM          | Original Equipment Manufacturer   |
| ORNL         | Oak Ridge National Laboratory of the Department of Energy - Oak Ridge, TN   |
| PDU          | Process Development Unit - a scaled version of a steam reformer used to conduct pilot testing   |
| PH           | Pulse Heater - usually followed by 2 numbers [PH 1-3] designating the location of the heater. The first number indicates the reformer and the second number indicates the position with number 1 at the bottom and number 4 at the top of a reformer. |
| pph          | Flow in Pounds Per Hour   |
| Project XL   | Project eXcellence and Leadership - an EPA “stakeholder” process to develop innovative approaches to environmental protection   |
| psig         | Pressure in Pounds per Square Inch - Gauge  |
| RPG          | Reformer Product Gas - the fuel gas produced by the steam reforming process   |
| StoneChem    | Baltimore, MD - TRI Division for North America for Pulp & Paper Applications  |

|       |   |
|-------|---|
| TAPPI | Technical Association of the Pulp and Paper Industry - Atlanta, GA  |
| TRI   | ThermoChem Recovery International - Baltimore, MD - Exclusive Licensee<br>(except India) for Pulp & Paper Applications of the MTCI technology |
| UMR   | University of Missouri-Rolla - Rolla, MO  |
| VADEQ | Virginia Department of Environmental Quality  |
| VOC   | Volatile Organic Compounds - an air pollutant identified in the MACT II<br>regulations  |

## **PROJECT DESCRIPTION**

The project conducted by Georgia-Pacific LLC was a comprehensive, complete commercial-scale demonstration of the MTCI PulseEnhanced™ black liquor steam reformer chemical recovery technology that was divided into two phases. Phase I was the validation of the project scope and cost estimate. Phase II was the project execution, data acquisition and reporting, and consisted of procurement of major equipment, construction and start-up of the new system. Phase II also included operation of the system for a period of time to demonstrate the safe operation and full integration of the energy and chemical recovery systems in a commercial environment.

The objective of Phase I was to validate the process design and to engineer viable solutions to any identified technology gaps. This phase included engineering and planning for the integration of the steam reformer system into GP's operating pulp and paper mill at Big Island, Virginia. During this phase, the scope and cost estimate was finalized to confirm the cost of the project including integration into the existing system at the mill.

The objective of Phase II of the project was the successful and safe completion of the engineering, construction and functional operation of the fully integrated full-scale steam reformer process system. This phase included installation of all associated support systems and equipment required for the enhanced recovery of both energy and chemicals from all of the black liquor generated from the pulping process at the Big Island Mill. The objective also included operation of the steam reformer system to demonstrate the ability of the system to operate reliably and achieve designed levels of energy and chemical recovery while maintaining environmental emissions at or below the limits set by the environmental permits.

## SUMMARY

Georgia-Pacific LLC undertook this project as a means of bringing the Big Island Mill into compliance with MACT II Environmental Regulations. The mill's black liquor smelters did not meet MACT II VOC emissions limits and the intent was to replace the smelters with the MTCI PulseEnhanced™ Gasification technology. Since there were no full scale commercial applications of the technology in service, there was a risk that the technology would not meet the environmental or financial criteria necessary for continued operation of the Big Island Mill. To mitigate the environmental risk, GP entered into a Project XL agreement with the EPA, VADEQ, and the U.S. Department of Agriculture Forest Service in May 2000. The agreement provided GP three years from finalization of an Agreement with DOE to build and start up a new conventional recovery boiler to replace the existing smelters if the project were determined to be unsuccessful. Later, the VADEQ granted GP a one year extension of the technology decision date to March 2005. In February 2005, VADEQ issued a consent order to GP providing an additional 2 year extension to the technology decision date. Under the terms of the consent order, the decision to accept or reject the technology had to be made by March, 2007.

To help mitigate the financial risk for the project, GP applied for DOE funding. An engineering study into black liquor gasification and the MTCI PulseEnhanced™ Gasification technology was funded under DOE Contract DE-FC07-99ID13818. In February 2001, GP was awarded DE-FC22-01NT40850 by the DOE for the full scale demonstration project. Appendix 7 includes the project spending and DOE funding information. In October 2001, DOE released GP for Phase 2 of the project which included construction and demonstration of the technology. Construction was started October 2001. During the detailed engineering of the project a series of "What If" reviews were conducted with the project team, GP operations and maintenance personnel and suppliers. As a result of these reviews, process changes were required to make the process safer. This resulted in design changes which required additional engineering and several equipment changes which caused some construction delays. Instrumentation checkout was started September 2003 and system flush and commissioning was started the next month. System commissioning was completed and the first liquor was injected into Reformer 1 on March 6, 2004.

In June 2003, GP entered into an agreement with Norampac in Trenton, Ontario, Canada and StoneChem to share information on the safety, operation and maintenance of steam reformers. Norampac was in the process of starting up a unit similar to the GP steam reformers. The sharing of information continued throughout the project. To provide the readers of this report a total perspective of where the steam reforming technology stands after the completion of the GP project at Big Island, DOE has provided Appendix 8 "Summary of Steam Reformer Safety, Operational and Maintenance Experience and Achievements at Norampac" based on input from TRI, Inc.

From March 2004 through August 2006, 24 separate liquor runs were conducted. Appendix 4 to this report includes the sections of the quarterly reports with the details of the individual liquor runs. During these liquor runs, it was determined that the fluidization of the bed was not adequate to support the process. In June 2004, the process to redesign the fluidization grid for the reformers was started. A scaled physical model of the steam reformer was constructed at PEMM



Corporation as a collaborative effort between GP, Norampac and TRI. Several grid designs were tested over a 3 month period. Modifications to the fluidizing grids of the reformers were implemented several times on subsequent liquor runs. Additional modeling at PEMM was conducted in January 2005 and further improvements made to the fluidization system. These changes made it possible to maintain fluidization in the heater bundles and no further attempts were made to improve system performance by optimizing the design of the fluidizing grid. The final grid used in the reformers is shown in Appendix 6.

Significant changes and trials were also conducted on the liquor injectors in an attempt to improve the liquor distribution and injector reliability while reducing the tar formation and improving the carbon conversion in the bed. Trials with various designs of injectors, sizes of injector tips, and variations of spray patterns were conducted. Individual flow meters for each injector were tested and installed to better control liquor distribution. At the end of the project, testing at the University of Utah was still in progress on injectors. The results of this will be reported by the University of Utah or TRI upon completion of the work. None of the liquor injectors trialed by GP resulted in any significant improvement in carbon conversion or a reduction in tar production.

As issues affecting the operability of the process were discovered during the liquor runs, they were addressed for subsequent runs. A redundant bed removal system was installed, methods for unplugging liquor injectors and the bed unloading nozzle were designed and spare pumps were added to the gas clean up system. A system of 'dummy tubes' equipped with multiple thermocouples was installed in all pulse heaters to warn of plugging and overheating problems on the bed side of the heaters. The combustion chamber refractory was replaced several times. GP determined the cause of refractory failure was due to overheating. A modification to the combustion air system and improvements to the instrumentation were successful in preventing further refractory failures. The failure of the aerovalve tips due to overheating was analyzed and addressed by upgrading the aerovalve design and the metallurgy. The new design appeared to have solved the problems.

During several of the liquor trials, problems were experienced with the pulse heater exhaust ducts and expansion joints. The original design was a carbon steel duct with an internal low density refractory lining and exterior insulation. Failure of the refractory lining in the elbows led to failure of some of the expansion joints. These elbows were replaced with stainless steel duct and new expansion joints. Later, the refractory in vertical sections of the duct as well as the new expansion joints began to fail. At the end of the project, GP was in the process of replacing all of the exhaust ducts with stainless steel duct.

In August 2005, GP attempted simultaneous operation of both reformers for the first time. Both units were operated and processed liquor at rates between 60% and 80% of the plant design rate for a period of 8 days. The run was terminated because the gas cleanup system plugged with tar. This was the first time tar fouling of the gas clean up system was the primary cause of shutting the units down. During the project, numerous steps were taken to reduce the impact of tars on the gas cleanup system including installation of additional pumps and strainers, increasing the system purge, modification of the process flow, and the addition of a chemical dispersant to keep the tars in suspension. Samples of the tar material were collected and analyzed, an analytical study of the tar formation was conducted by the IPST, and pilot trials were conducted by KMPS

for design of a tar capture and removal system. At the end of the project, the trials for the removal system and the system design had not been finalized.

During the project, GP experienced failure of the in-bed pulse heater thermocouples used to control the firing rate of the heaters. The action of the fluidized bed would damage the thermocouples and cause the heaters to trip off line. By the end of the project, these thermocouples could no longer be used and control of the pulse heater firing rate was based on combustion chamber temperature and the readings of the dummy tube thermocouples installed to detect bed side plugging of the heater bundles. The action of the bed also damaged the upper heater in both reformers. GP modified the heaters in this position to eliminate the mid-point baffle support rods and supported the baffle from the tube bundle. All of the mid-point baffles were trimmed to eliminate excess surface area and minimize the problems. A picture of a pulse heater is shown in Appendix 5.

Beginning in March 2006, GP discovered leaks in the tube sheets of the pulse heaters. At first these appeared to be random and were attributed to manufacturing errors. As the problem became worse, samples of the cracked material were analyzed to determine the cause. Metallurgical examination of the failures indicated the mechanism to be caustic assisted stress corrosion cracking. The root cause is not known. Seven of the eight heaters experienced tube leaks with one unit experiencing a severe problem. It was concluded that the availability/reliability of the system would continue to deteriorate due to increasing failure rates on the pulse heaters and redesign and replacement of the heater assemblies would be required before the system could restart.

At the end of the final trials, a detailed inspection of all of the pulse heaters was conducted. Several other issues with the pulse heaters were identified or reexamined. A previous problem with bowing of the tubes in the pulse heaters was reviewed and found to be increasing slightly. Significant bowing of the exhaust tube sheets was also found. Cracking of the tube ends at the exhaust tube sheet which was discovered on previous inspections was still evident.

In October 2006, the status of the project was reviewed with G-P senior management. It was concluded that the availability/reliability of the steam reformer system would not be adequate to support continued operation of the Big Island Mill by the March, 2007 deadline in the VADEQ consent order and the decision was made to terminate the project and proceed with installation of conventional recovery boiler technology for processing the mill's black liquor.

## DISCUSSION AND RESULTS

During the project, the availability of the reformer system started out low but gradually improved over time. The project experienced a significant number of equipment failures of auxiliary equipment which were not related to the basic technology. Resolution of these issues consumed some of the time needed to fully evaluate the technology. Since these issues, such as pump failures, damper failures, etc., are not related to the technology implementation, they will not be discussed in detail.

Several issues were encountered that were related to the basic reformer technology. The carbon conversion attained was below the predicted value. The production of reformer product gas (syngas) was below predicted while the production of condensable hydrocarbons (tars) was higher than predicted. The pulse heaters did not achieve the predicted heat transfer to the bed. As a result of these issues, the overall energy conversion efficiency of the process was below predicted. The reliability of the technology was also significantly below expectations. Not including the early failures listed above, numerous mechanical and instrumentation problems limited the run time on liquor. The reliability was gradually improving over time until the pulse heater failures reversed the trend.

As stated above, the thermal efficiency of the project was below predicted values. As shown in Appendix 3, about 50.3% of the total energy supplied to the process was lost. The major short-falls included the losses at the reformer boiler for (36.5%), cooling tower (23%), tar lost fuel value (16%), bed carbon (9%) and gas cleanup system purge (8%). The losses at the reformer boiler were higher than expected due to higher than predicted excess air and higher than predicted flue gas flow from the pulse heaters. The pulse heaters were fired with higher than predicted excess air to protect the refractory and control the temperature in the exhaust plenum. Cooling tower losses were higher than predicted due to the excess of fluidization steam required by not utilizing recycled reformer product gas for part of the fluidization. The tar losses were higher than predicted due to the larger amount of tars produced. These tars were condensed in the gas cleanup system and sent to the effluent treatment ponds. The bed carbon loss was higher than predicted due to the reduced carbon conversion experienced. The lower carbon conversion resulted in more carbon leaving with the bed solids and being filtered in the green liquor filter. The gas cleanup purge losses were higher than predicted due to an increase in purge flow to help purge the condensed tars from the gas cleanup system. Many of these items will be discussed in greater detail in the remainder of the report.

The process issues of the technology are not necessarily independent of one another. Carbon conversion, tar production, bed particle size and pulse heater heat transfer to the reformer bed are all related to some extent. GP conducted trials with various liquor injector designs to judge the impact of liquor distribution on the process. Although some impact could be seen, the changes were not significant enough to resolve the issues. Although not tested, it is possible that increasing the number of injectors and spreading them over the cross section of the bed could improve performance. GP did not attempt to relocate injectors due to the cost and complexity of modifications to a refractory lined pressure vessel. Liquor injection properties such as injection pressure and temperature, percent solids of the liquor and amount of injection steam used were

varied in an attempt to achieve better liquor distribution. The fluidization of the bed also has an impact on these issues. GP experimented with several fluidization grid designs in the full scale unit as well as in the scale model. Once a grid that was capable of moving the bed solids through the heater and eliminating the tendency for the heaters to plug was proven, further changes to the grid to improve process performance were not attempted. GP varied the fluidization steam velocity, height of the fluidized bed as well as the bed temperature to determine if any improvement could be achieved. These changes did not produce significant improvement.

The lower than design carbon conversion affected the performance of the green liquor filter. Due to the high solids loading, the filter could not sustain operation at full mill capacity. GP had planned to replace the existing unit with a unit sized for the higher solids loading. The carbon from the filter would have been taken to the landfill until an environmental permit modification could be obtained to use it as fuel in one of the mill's boilers. The project was terminated before the filter was replaced.

The reliability of the process was impacted by several factors. Early in the liquor runs, pulse heater plugging due to the fluidization system and the start up bed were key issues. GP implemented a grid design modeled at PEMM and later revised the design when it became apparent that the limestone used for start up of the unit was also an issue. From that point forward when start up bed was required, it was purchased from the Norampac facility. Once the pulse heater plugging issue was eliminated, problems were encountered with the internal cyclones used to prevent solids carryover to the gas cleanup system. These did not appear to be as efficient as predicted so the dip legs were extended deeper into the bed. Even with additional bracing on these dip legs, the forces from the bed movement caused these to fail. Based on experiences at PEMM and discussions with the cyclone supplier, the dip legs were shortened to terminate above the fluid bed and modifications were made to the cyclone inlets and outlets. This resolved the issue with the cyclones.

The next group of issues encountered was failures of the refractory in the pulse heater combustion chambers. Much research was conducted on this issue with help from the University of Missouri-Rolla and ORNL. The root cause of the problem was finally determined to be overheating. The pulse heater combustion chamber thermocouples were installed approximately flush with the inside refractory and tended to provide artificially low readings. New thermocouples were installed that extended into the combustion chamber to provide a better indication of combustion chamber temperature. The refractory life improved, but due to limited run time after this change, the results were not fully evaluated.

After resolution of these issues, the process was able to run for longer periods. Once the system operation was extended, the issues with the gas cleanup system began to appear. Tar accumulation in the venturi demisters, gas cooler heat exchangers, gas cooler packing and in the pump strainers caused significant down time. Operations was able to run at rates below 70% of the liquor processing rate for extended periods, but was not able to achieve higher throughput on a continuous basis. A chemical dispersant was effective in reducing the tar buildup in the wetted areas, but was not effective in the gas phase. As the heat exchangers began to foul, the gas cooler effectiveness was reduced to the point the system had to be shut down for cleaning. GP began the pilot testing and engineering study for implementation of a tar collection and recovery

system. The intent was to recover the tars and burn them as a liquid fuel in the reformer boiler. Burning the tars as fuel would have required a modification to the environmental permit.

In addition to the problems resulting from the fouling of the gas cleanup system, it was determined that the cooling tower capacity of the system was not capable of full load operation. The heat load to the system was higher than design due to the increased fluidization steam used by the system. The original design was based on recycling a portion of the product gas to the fluidizing grid to reduce the steam required. Testing at the University of Utah and at IPST indicated the use of recycle gas could inhibit the carbon conversion and further increase tar production. The system to recycle product gas was never tested during the project.

After TRI notified GP about potential overheat damage to the aerovalve assemblies at Norampac, the GP aerovalves assemblies were inspected and wastage and cracking was found. GP installed thermocouples on the tips of several aerovalves and readings indicated the operating temperature of the metal was significantly higher than the design point and exceeded the allowable temperature for the metal. GP provided TRI with a preliminary design and material selection for the redesign of the aerovalves. The units were redesigned and GP had new units fabricated. Testing of the first unit indicated the metal temperatures were well below maximum under all operating conditions. The project ended before all eight of the aerovalve assemblies could be installed and fully tested.

Throughout the project GP experienced problems with the liquor injection system. Some of these problems were due to experimentation with various designs in order to improve performance. The primary problem with the injectors was plugging. Injectors would plug with bed solids or with liquor. GP developed a procedure to unplug the injectors by drilling and later adopted a water blasting method used at Norampac. Cleaning of the injectors was not successful in many cases. At the end of the project, GP still had reliability issues due to injector plugging.

The pulse heater exhaust ducts were also a significant problem during the project. The internal refractory system used for the duct did not perform as required. This resulted in lost time for liquor runs. Prior to the end of the project, GP redesigned the duct to be stainless steel with no internal refractory. All of the expansion joints were also redesigned. The project ended before this change could be implemented.

While the last liquor runs were in progress, GP attended a meeting with Norampac and TRI to review pulse heater issues and proposed design changes. Based on the discussions during the meeting, GP inspected the pulse heater exhaust tube sheets and found bowing to be a problem not discovered prior to this inspection. GP also inspected the pulse heater tubes for bowing and determined the problem was slightly worse than in the past. Hydrostatic test of the pulse heater tube sheet on one unit indicated a large quantity of through-wall cracks (over 20) on the combustion chamber side and some leaks on the bed side tube sheet. Failure of the bed side tube sheet would make repair of the unit very costly due to lack of access. GP also discovered one of the heaters had sustained some overheat damage to the tubes due to failure of the tips of some of the original aerovalves. It was concluded that the availability/reliability of the system would continue to deteriorate due to increasing failure rates on the pulse heaters and redesign and replacement of the heater assemblies would be required before the system could restart.

As noted previously, the status of the project was reviewed with G-P senior management in October 2006. It was concluded that the availability/reliability of the steam reformer system would not be adequate to support continued operation of the Big Island Mill by the March 2007 deadline in the VADEQ consent order and the decision was made to terminate the project and proceed with installation of conventional recovery boiler technology for processing the mill's black liquor.

## EXPERIMENTAL

GP conducted various trials on the reformers during the liquor runs. These trials are covered in detail in the descriptions listed in Appendix 4. The primary purpose of the trials was to improve the reliability of the process to allow longer runs at stable operating conditions closer to the design level. The secondary purpose was to improve the carbon conversion and reduce the production of tars. Trials were conducted to vary the liquor injection parameters as well as test various designs of injectors. Although some impact of these changes was noted, overall GP was not able to significantly improve either of these problems. Other operating parameters were also varied such as bed height, fluidization velocity, and bed and fluidizing steam temperature to the extent practical. These variables had less of an impact than the liquor injection changes.

GP also conducted various trials to improve the reliability of the system. Most of these trials were site specific to the GP installation. These trials were used to determine the impact of steam temperature on the lower bed temperature, the variation in pulse heater combustion chamber temperature across the combustion chamber, and the effect of RPG moisture on the reformer boiler combustion.

Modeling of the reformer fluid bed was conducted at PEMM, Corp. using a physical scale model of the reformer vessel and a screened limestone bed. This modeling effort was a collaborative effort between GP, Norampac, and TRI. This model was used to design various grids which were later trialed at GP in full scale.

In a collaborative effort with Pavilion Technologies, Norampac and TRI, GP attempted to develop neural network models of the process variables which affected carbon conversion and bed particle size. This effort was not successful due to the limited frequency and testing variability of the bed solids for size distribution and carbon content. Another problem with development of the models was the inability to vary the process variables widely enough to define the models.

GP conducted several trials to find a suitable refractory for the combustion chamber of the pulse heaters. This research was driven by the failures which were later determined to be primarily caused by overheating. Several refractory suppliers, the University of Missouri-Rolla, ORNL, Norampac, and TRI collaborated on this effort.

Early in the project, GP discovered the 321 stainless steel tubes of the pulse heaters were experiencing severe carburization. Working with ORNL, LBNL, Georgia Tech and Fluor, it was determined that the carburization would not lead to immediate failures of the tubes. In an effort to find a more suitable material for this application, GP had two full length tubes of each of eight different material alloys placed in a pulse heater. The intent was to expose these tubes to operating conditions and later examine them at intervals to determine if any of these alloys proved better suited for the application. Final disposition of the sample tubes had not been determined at the time this report was written.

GP and TRI funded a study conducted by the IPST to study and quantify the formation of tars in the steam reformer. The study included laboratory trials using liquor from Big Island as well as field sampling of tars from the operating unit. The results of this study were included in the paper “Measurement of Tars Produced during Low-Temperature Black Liquor Gasification” presented at the TAPPI Engineering Conference in 2006. GP also contracted KMPS to perform pilot trials to design a tar removal and collection system. The pilot trials were conducted and indicated removal of the tars from the gas clean up system was feasible. The final trials and system design were not completed prior to the end of the project.

At the project end, the University of Utah was still conducting trials utilizing their PDU to test a liquor injector designed by TRI. This was a collaborative effort between TRI, Norampac and GP. Results of these trials were not available when the report was issued.

During the project, GP also supported several DOE funded research programs. These included:

- DE-FC26-02NT4 1490 – University of Utah project “Investigation of Fuel Chemistry and Bed Performance in Fluidized Bed Black Liquor Steam Reformer”
- NETL Project – NT02.2 “Fuels Chemistry”
- NETL Project – NT02.3 “Fuels Chemistry”
- NETL BL/Biomass Gasification – Mill Integration Effort – Yocum
- NETL BL/Biomass Gasification – BL Containment – Chaddock
- ORNL Materials Evaluation for Black Liquor Gasifiers – Keiser
- MTCI Liquor Injection/Tar Formation Study – Chandran
- Modeling Working Group – Keairns



## **CONCLUSION**

This project was not able to operate at a steady state long enough for the technology to be evaluated completely. Significant issues still remained at the end of the project as listed in the sections above. GP made the business decision to terminate the project in favor of conventional technology. Many factors were evaluated in this decision process, including the short time remaining before the required technology acceptance date, the cost of implementing the changes identified, and the uncertainty of the success of all of these changes. Since this demonstration project was intended to replace the existing recovery technology at the Big Island Mill, any future issues would have adversely affected the productivity of the mill.

## **PATENTS AND PUBLICATIONS**

The GP project team did not apply for any patents related to this project or technology. The GP project team did not publish any articles or material as part of this project. The project team did contribute to articles published by others such as the Department of Energy – Oak Ridge National Laboratory, the University of Utah and the Institute of Paper Science and Technology.

## **ACKNOWLEDGEMENTS**

Georgia-Pacific LLC would like to acknowledge the Department of Energy for the funding provided for this project and for the assistance of NETL and ORNL on research issues.

GP would like to thank the EPA Project XL stakeholders including EPA, Virginia DEQ, the US Department of Agriculture Forest Service and citizens from the local community for their time and support during the project.

Thanks to the research conducted by the University of Utah, Brigham Young University, the University of Toronto, the University of Missouri-Rolla, and by the Institute of Paper Science and Technology, significant improvements were made in this project.

Special thanks to the personnel at Norampac for sharing ideas and experiences in a collaborative effort to resolve many problems.

Georgia-Pacific LLC would like to acknowledge the personnel from StoneChem and ThermoChem Recovery International for providing design assistance, technology support and for assistance during the start up, commissioning and liquor runs on this project.

Georgia-Pacific LLC would like to acknowledge the personnel from Fluor who provided the detailed design engineering for the plant and assisted with process engineering throughout the commissioning effort and liquor runs.

## Appendix 1

|   | Comparative Percentages |           |                 |
|---|-------------------------|-----------|-----------------|
|   | Steam Reformer          |           | Recovery Boiler |
|   | Demonstrated            | Predicted | Predicted       |
| Percentage of Target Capacity of the Steam Reformer                           | 72.5%                   | 100.0%    | 100.0%          |
| Percentage of Target Gas Production Rate                                      | 42.4%                   | 100.0%    | N/A             |
| Percentage of Target Gas Production Rate Adjusted for Actual Liquor Processed | 58.5%                   | N/A       | N/A             |
| Percentage of Target Gas Higher Heating Value                                 | 139.6%                  | 100.0%    | N/A             |
| Quality of Reformer Bed Material Discharge - (Bed Carbon Content)             | 8.0%                    | 1.2%      | N/A             |
| Steam Reformer Carbon Conversion  | 86.1%                   | 99.0%     | N/A             |
| System Overall Thermal Efficiency   | 49.7%                   | N/A       | 67.8%           |

### Notes:

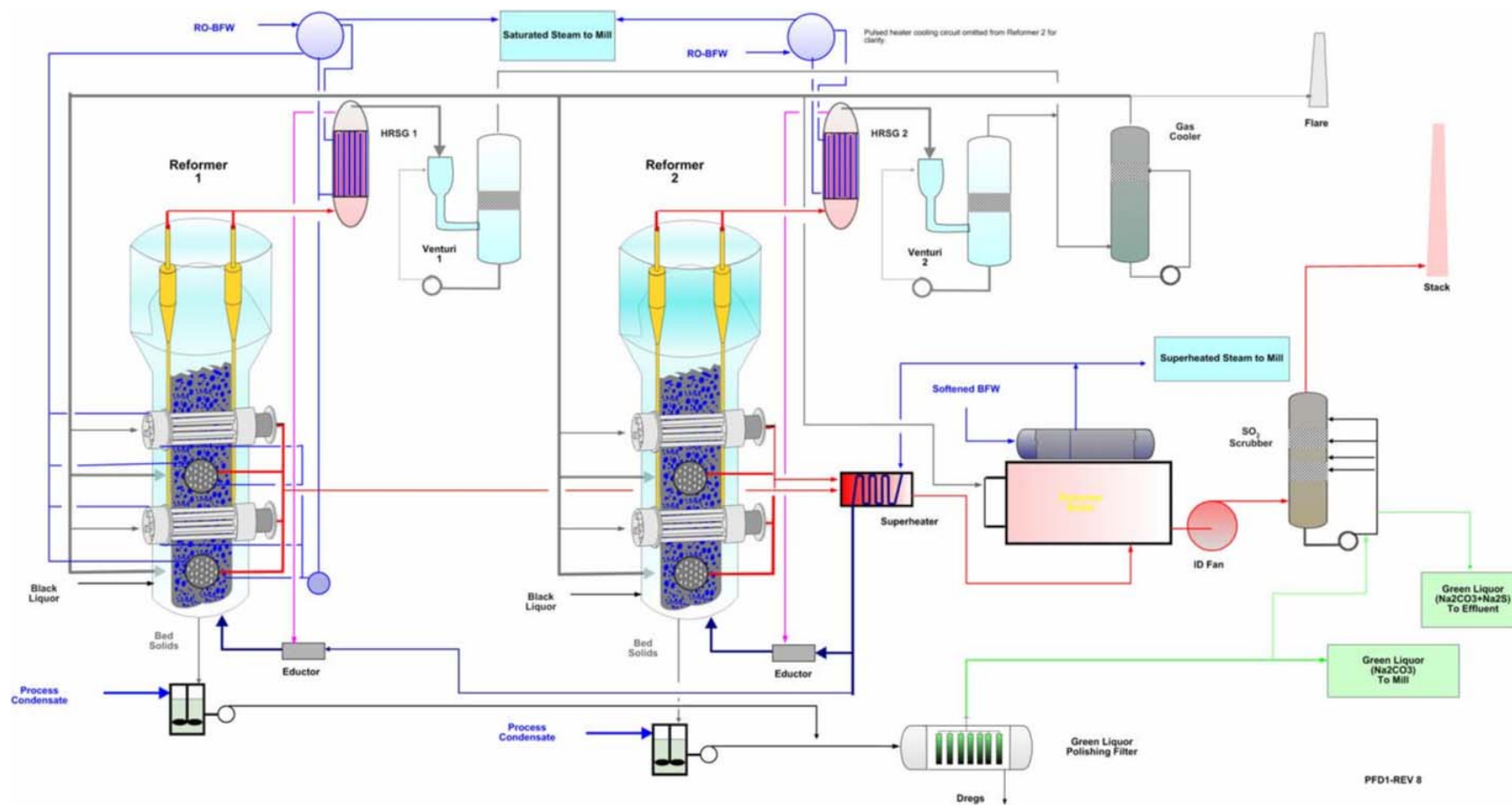
Demonstrated values were taken from the evaluation calculation for liquor runs 20 and 21 on 5/18/06 from 4 a.m. to 11 a.m.

Predicted values for the steam reformer were taken from StoneChem contract.

Predicted values for the recovery boiler were taken from predicted performance supplied by boiler manufacturer for unit for this facility.

## Appendix 2

### Simplified Process Flow Diagram



### Appendix 3

| Simplified Balance Based on Liquor Runs<br>20 & 21 on 5/18/06 between 4am-11am |          |                  |                         |                      |  |   |                                |                            |                         |
|--|----------|------------------|-------------------------|----------------------|--|---|--------------------------------|----------------------------|-------------------------|
|  |          |                  |                         |                      |  |   |                                |                            |                         |
| 65.70  | mmbtu/hr | Black Liquor HHV | →                       | Steam Reformer Plant |  | → | HP Steam                       | 86.27                      | mmbtu/hr                |
|  | 30       | gpm              | Approximate Flow        |                      |  |   | 58000                          | pph                        | Approximate Flow        |
|  | 65       | psig             | Approximate Pressure    |                      |  |   | 600                            | psig                       | Approximate Pressure    |
|  | 250      | F                | Approximate Temperature |                      |  |   | 950                            | F                          | Approximate Temperature |
| 20.32  | mmbtu/hr | Boiler Feedwater | →                       | Steam Reformer Plant |  | → | HP Saturated Steam             | 17.79                      | mmbtu/hr                |
|  | 170      | gpm              | Approximate Flow        |                      |  |   | 15000                          | pph                        | Approximate Flow        |
|  | 270      | F                | Approximate Temperature |                      |  |   | 550                            | psig                       | Approximate Pressure    |
|  |          |                  |                         |                      |  |   | 480                            | F                          | Approximate Temperature |
| 31.92  | mmbtu/hr | Fluidizing Steam | →                       | Steam Reformer Plant |  |   | Total                          | 104.06                     | mmbtu/hr                |
|  | 23000    | pph              | Approximate Flow        |                      |  |   |                                |                            |                         |
|  | 30       | psig             | Approximate Pressure    |                      |  | → | Losses                         | 105.23                     | mmbtu/hr                |
|  | 900      | F                | Approximate Temperature |                      |  |   | Calculated Breakdown of Losses |                            |                         |
| 91.35  | mmbtu/hr | Natural Gas      | →                       | Steam Reformer Plant |  |   | 23%                            | Cooling tower              |                         |
|  |          |                  |                         |                      |  |   | 36.5%                          | Boiler                     |                         |
|  |          |                  |                         |                      |  |   | 2.5%                           | HRSG                       |                         |
|  |          |                  |                         |                      |  |   | 8%                             | Gas Cleanup System Purge   |                         |
| 209.29   | mmbtu/hr | Total            |                         | Steam Reformer Plant |  |   | 9%                             | Bed Carbon / Sensible Heat |                         |
|  |          |                  |                         |                      |  |   | 16%                            | Tar                        |                         |
|  |          |                  |                         |                      |  |   | 5%                             | Radiation                  |                         |
|  |          |                  |                         |                      |  |   | 100%                           | Total Losses               |                         |

## **Appendix 4**

### **Report 40850R13 for the period from 1/3/04 through 4/2/04**

During this reporting period, all of the systems necessary to operate Reformer 1 were commissioned. The systems remaining to be commissioned are the Reformer 2 and the Green Liquor systems. The project plans to operate Reformer 1 to discover and implement necessary changes, prior to operating Reformer 2. The Green Liquor system will be commissioned as soon as suitable bed solids can be produced. Since the initial bed is limestone, a significant period of operation is required to convert the bed to sodium carbonate suitable for production of green liquor.

The following systems or major areas were commissioned:

- Heat tracing and insulation.
- Initial firing of the Pulse Heaters on natural gas and curing Pulse Heater Refractory.
- Black liquor supply and delivery system.
- Bed media transport system.
- Reformer bed solids lock hopper system.
- Fluidizing steam superheater.
- Chemical cleaning of the waterside of the HRSG's and Pulse Heaters.
- Full scale firing of the Pulse Heaters on natural gas.
- Initial process commissioning runs with black liquor.
- Operation of the Flare with reformer product gas.

### **Report 40850R14 for the period from 4/3/04 through 7/3/04**

During this reporting period, the project operated Reformer 1. The experience from Reformer 1 will be used to implement necessary changes prior to operating Reformer 2.

The following systems or major areas have not been commissioned:

- Reformer 2 systems
- Firing of product gas in the Pulse Heaters.
- Firing of product gas in the Reformer Boiler.
- Green Liquor Filter

Pulse Heaters 1-1 and 1-2 were shipped to the OEM for repair. These will be repaired and returned during the next reporting period.

The modifications that were proven successful on Reformer 1 were implemented on Reformer 2. This included modification to the liquor injectors to reduce their internal diameter. During the next liquor trial, injectors of 2 smaller diameters will be evaluated. GP also plans to evaluate a new injector design with a steam-atomized tip.

Modifications of HRSG steam piping were implemented to control the fluctuations of steam drum level caused by swings in the 600 psig steam header. Additional modifications were made to move the location where the steam enters the header to eliminate the cooling of the fluidization steam supply to the fluidization grids.

The bottom bed solids drain from the vessel has been modified into a manual bed removal system to be used during operation. This system will be used to remove oversized bed material that segregates in the bottom of the vessel. During the next liquor trials, this system will be used to evaluate the need for an automated bottom bed removal system.

Modifications were made to the supports for the piping and ductwork attached to the Reformer vessels. These modifications were necessary due to the extent of the vessel movement during operations.

### **Report 40850R15 for the period from 7/4/04 through 10/2/04**

During this reporting period, the project installed a new fluidization grid in Reformer 2. All systems associated with Reformer 2 were commissioned. The refractory in the Pulse Heaters of Reformer 2 was cured and the vessel was started up. During the liquor trial the unit operated at approximately 50% of the design liquor injection rate with periods as high as 70%. The liquor trial was terminated due to evidence of plugging in Pulse Heater 2-1. The cause of the plugging is still under review but appears due to loss of fluidization within the core of the PH2-1. The loss of fluidization resulted from a decrease in bed particle size and reduced fluidization steam flow resulting from a flow measurement error.

Additional instrumentation was added to Pulse Heater 2-1 to help monitor the effectiveness of the fluidization system within the heater. Four 'dummy tubes' were created by plugging pulse heater tubes on the firing end. Thermocouple assemblies consisting of four thermocouples were inserted in each dummy tube to measure the temperature of the bed material in various locations along the length of the tube. During the subsequent liquor trial, the dummy tube thermocouples detected heater plugging and the heater was shut down immediately. Later inspection of the pulse heater confirmed the thermocouples had correctly identified the presence of plugging and prevented overheating of the heater tubes.

During the liquor trial, liquor injectors of 2 smaller diameters as well as a steam atomized injector were evaluated. The small diameter liquor injectors did not perform effectively due to plugging problems. The steam atomized injectors appeared to function well, but the evaluation was not completed. Additional steam atomized injectors will be installed and the evaluation will continue on future liquor trials.

HRSG steam piping modifications were evaluated and determined to be effective in controlling the fluctuations of steam drum level caused by swings in the 600 psig steam header. The modifications eliminated the cooling of the fluidization steam supply to the fluidization grids.

A new bed solids drain was installed on the bottom of the reformer and was partially automated. During future liquor trials, the project will evaluate the need to incorporate this system into the green liquor recovery system.

An air heater was added to the fluidizing air system. This system was commissioned and used in the start-up and refractory cure process for Reformer 2. The air heater system performed better than expected and was very beneficial in the start-up process.

The green liquor filter was commissioned and operated to process green liquor for the mill. During the commissioning, the filter had to be removed from service, inspected and modified two times. Modifications were required due to the nature of the material produced in the dissolving tanks. Prior to this liquor trial, liquor of this type had not been available to test filters.

Pulse Heaters 1-1 and 1-2 were repaired by the OEM and returned to the project. These were installed in Reformer 1 and are being made ready for operation.

The following systems or major areas have not been commissioned:

- Firing of product gas in the Reformer Boiler.
- Firing of product gas in the Pulse Heaters.

#### **Report 40850R16 for the period from 10/3/04 through 1/1/05**

During this reporting period, two trials were conducted using Reformer 2. The first trial [Trial 6] was started on October 4 and was terminated on October 6 prior to the injection of liquor. During the start-up cycle problems were encountered with plugging of the bed media transfer system, the lock hopper bed removal system and several of the level indication taps. In addition, steam fluidization flow measurement error caused the fluidization to be below target. Some indications of plugging in PH2-1 appeared so the decision to shut down was made.

The second trial [Trial 7] on Reformer 2 was started on October 18 and was terminated on November 19. Liquor was processed for 25 days during a 28 day period. The liquor processing rate during this period reached up to 85% of the design rate for one vessel. During this run, the unit was taken off line twice to repair expansion joints on the pulse heater flue gas exhaust duct. Plugging was detected in PH2-1 6 days after the start of the run and the heater was not used for the remaining time. Various trials were conducted to determine the impact of the steam atomized liquor injectors on bed solids particle size and on pulse heater operation. It was determined that the atomized liquor injectors, as designed, increased the bed solids carry over.

With fluidizing grid GP-2, the fluidization steam is concentrated in the area directly under the pulse heaters. The 'corners' of the unit have less fluidization in order to promote downward flow of bed solids. Since a significant portion of the liquor injection takes place in the downward flow region, changes in liquor flow affected the fluidization. This resulted in pulse heater trips and reduced firing rates. PH2-2 experienced the most impact from the liquor injection changes. With a reduced firing rate for the pulse heaters, the liquor injection rate also was reduced. The unit was operated in this fashion for several days while other trials were conducted. During

periods of liquor injection below 50% of capacity, the baseline attrition of the unit causes the bed solids particle size to decrease. This decrease has an adverse impact on both fluidization and bed solids carryover. Based on the limited liquor processing capability and high bed solids carryover, the unit was taken off line.

Inspection of Reformer 2 after Trial 7 identified several problems. PH2-3 experienced overheat tube failures of 14% of the tubes caused by loss of fluidization and bed agglomeration in the core of the unit. Build up of bed solids was also evident in PH2-1 and PH2-2 as well as on the ends of most liquor injectors. NDE inspection of the aerovalves identified cracking at the ends of the many aerovalves in PH2-2, PH2-3 and PH2-4. The inspection identified a failure of the refractory in the combustion chamber of the pulse heaters along the tube sheets. Sections of the refractory sheared approximately at the midpoint of the refractory thickness.

A trial [Trial 8] on Reformer 1 was started on December 3 and was terminated on December 10. An extended start-up period was required in order to cure the new refractory of PH1-1 and PH1-2 installed when the units were repaired. Liquor injection began December 5 and reached a peak of 60% of the design rate. Prior to beginning the trial, all of the pulse heaters in this unit were equipped with 'dummy tube' thermocouples to measure the bed temperature in the core of the heaters. This unit also had a modified fluidization grid Grid GP-4. This grid is a version of Grid GP-2 with a more uniform distribution of the spargers. GP-4 has the same number of spargers and design specifications, only a different distribution pattern. A second lock hopper bed solids removal system was added. All liquor injectors were the original concentric tube design (no steam atomized injectors were installed). The internal tube thermocouples indicated lack of fluidization in all pulse heaters except PH1-4. PH1-2 and PH1-3 showed indications of bed solids plugging. During the entire trial, the unit experienced high levels of bed carryover to the venturi.

Inspection of Reformer 1 after Trial 8 confirmed PH1-1, PH1-2, and PH1-3 had plugged areas. A water leak in the tube sheet of PH1-2 was also found to be leaking into the combustion chamber.

The only system not yet commissioned for the project is the firing of product gas in the Pulse Heaters. This activity will be deferred until stable operation of the reformers can be achieved. The metallurgy issues of the pulse heater tubes and aerovalves must also be resolved prior this activity.

#### **Report 40850R17 for the period from 1/2/05 through 4/2/05**

During this reporting period, three trials were conducted using Reformer 1. Trial 9 was started on January 1 and was terminated on January 5 prior to the injection of liquor. During the start-up cycle problems were encountered with high temperatures in the bottom 3 pulse heaters. This indicated poor fluidization of the bed. The trial was terminated to avoid severe agglomeration of the bed solids in the heaters or damage to the tubes. The bed material used for the start-up of this trial was composed of approximately 50% limestone and 50% bed material from the Norampac steam reformer.



After trial 9, GP conducted additional cold flow modeling was conducted at Pemm, Corp. in order to determine if the fluidization could be improved. Modifications to the fluidizing grid as well as the interior geometry of the vessel were modeled. Modeling was also conducted on the internal cyclones to determine if the collection efficiency could be improved.

While the cold flow modeling was in progress, bed solids were shipped to Brigham Young University and to the University of Toronto. Bed solids from the Norampac steam reformer were also shipped for comparison. The University of Toronto confirmed the chemical properties of the bed solids should not smelt at the temperatures encountered in the steam reformer. At BYU a series of agglomerations tests were conducted which indicated that the agglomeration of the GP material occurred at a relatively low temperature. BYU determined the primary cause of agglomeration was due to the variation in bed particle size particularly the oversized limestone material. Based on the results of the BYU testing, GP elected to conduct the next trials using bed material from the Norampac steam reformer.

The second trial [Trial 10] on Reformer 1 was started on February 18 and was terminated on February 25. Prior to trial 10, the fluidizing grid was modified [Grid GP-6] to increase the pressure drop across the grid to ensure even distribution of the fluidizing steam. The cyclone dip legs were extended to bring them deeper into the bed and remove them from the turbulent area near the top of the bed level. The bed material used for start-up was obtained from the Norampac steam reformer. The start-up of the unit went well and pulse heater performance was better than on any previous run. The carryover of bed material to the gas cleanup system was also reduced. The trial was terminated early when the support bracing for the cyclone dip legs failed allowing the dip legs to fall on top of PH1-4. PH1-4 did not sustain any damage that required repair. Data collected during the shutdown portion of the trial indicated that reduced carryover could be accomplished with dip legs which terminate above the bed level.

The cyclone dip legs were raised above the bed level and Reformer 1 was prepared for service. Trial 11 began on March 5 and ended on April 4. Again the start-up bed used was from the Norampac steam reformer. During the trial, failures of 2 pulse heater exhaust expansion joints resulted in period of reduced or no liquor injection while the repairs were made. During the normal operating periods, the unit was operated at full load for periods of time. During full load operation it was discovered a significant amount of tar (condensable hydrocarbons) was condensing in the venturi scrubber. Also, the carbon conversion of the unit was extremely poor. Several process trials were conducted to determine if process changes could reduce the tar formation and improve carbon conversion. The trial ended when PH1-4 showed signs of plugging which occurred over a very short period of time. Inspection of the unit revealed failure of the refractory in the combustion chamber. Preliminary analysis suggests the refractory failure resulted in some plugged tubes which forced excessive combustion gases through other tubes. The hotter tubes led to bed agglomeration and ultimate failure of several tubes.

Preliminary inspection of the aerovalves discovered some cracks on the aerovalve tips. The reformer inspection will be completed and additional investigation will be conducted next period.

During trial 11, GP participated in an effort to resolve the combustion chamber refractory failure. A conference call on 3/24 included participants from University of Missouri-Rolla, Oak Ridge National Lab, TRI, MTCI, and Norampac. Additional work will continue through the next quarter.

#### **Report 40850R18 for the period from 4/3/05 through 7/1/05**

At the end of last period, run 11 was completed. At the end of run 11 a steam-out trial was conducted and data was collected and analyzed. During this reporting period, three trials were conducted using Reformer 2. During all three trials, the reformer was operated with only 3 heaters in service. The fourth heater had been removed and shipped to Mitternacht for tubing replacement. The fluidizing grid in Reformer 2 was modified to the configuration of Grid GP-4.

Run 12 was started on April 14 and was terminated on April 27. During run 12, Reformer 2 had 6 steam atomized liquor injectors and 6 vertically oriented non-atomized injectors. The trial was terminated before the steam atomized injectors could be placed in service. Several problems were encountered including a bearing failure of the combustion air fan, problems with PH2-4 flame detection, and high tube temperatures on PH2-3. Run 12 was terminated when the high tube temperatures in PH2-3 could not be cleared. Inspection of PH2-3 [PH7185-5] after the run revealed a small area had plugged near the combustion end tube sheet resulting in damage to 8 pulse heater tubes. These tubes were plugged. The combustion chamber hot face tube sheet refractory was replaced with a new design which incorporates Inconel 601 wavy – V anchors and AZ-10 refractory material. The unit was returned to service.

Run 13 was started on June 2 and was terminated on June 4. Loud banging noises were heard inside the vessel during the bed warm up period of the start up. Since these sounds were similar to the sound produced in Reformer 1 when the internal cyclone dip legs failed, the decision was made to shut down the unit. Internal inspection of the vessel did not find any cause for the noise. The unit was cleaned and made ready for service. No liquor was processed during run 13.

Run 14 was started on June 13 with liquor injection beginning June 16. As of the end of the reporting period, the run was still in progress. This run appears more stable than previous runs. The differential temperature in the pulse heater tubes is very low at less than 10 °F. Liquor injection is limited to approximately 65% of rated capacity because only three of the four pulse heaters are in service.

#### **Report 40850R19 for the period from 7/2/05 through 10/1/05**

At the end of last period, run 14 on Reformer 2 was in progress. Run 14 started on June 13 with liquor injection beginning June 16. The run was terminated on August 30 after 75 days. This was our longest liquor run to date. This run was more stable than previous runs. The differential temperature in the pulse heater tubes was very low at less than 10 °F. Liquor injection was limited to approximately 65% of rated capacity because only three of the four pulse heaters were in service. During this run, we were able to influence the growth of the bed particle size by variations in the liquor injection rate and atomizing steam flow. Also during this run, the operators were able to quickly recover from several trips caused by lightning storms, problems with

the gas clean up system caused by tar accumulation, and steam swings from the mill steam system. PH2-4 experienced several trips due to loss of control thermocouples. At the end of the run an internal inspection revealed that all of the thermocouples had failed due to failure of the baffle support rods. During this run, the refractory lining in the elbow sections of the pulse heater exhaust ducts showed signs of failure causing the external temperature to rise. The insulation on the outside of the duct was removed and cooling fans with misting sprays were used to cool the duct. This increased heat loss also had an adverse effect on the fluidizing steam temperature. Since Reformer 1 was still down at this time, the ducts on that unit were inspected and the failure of these was noted. The equipment supplier was called in to make temporary repairs prior to the start of run 15. During run 14, the Cooling Tower Fan tripped without alarming allowing the water in the circulation loop to exceed the allowable for the tower packing. A portable tower was used to continue run 14 while the tower packing was replaced.

Run 15 started on Reformer 1 on August 20 with liquor injection on August 22. This was the first time simultaneous operation of both reformers was attempted. During the warm up of Reformer 1, the colder exhaust from the pulse heaters reduced the fluidizing steam temperature from the superheater. This resulted in a significant increase in the formation of tars from Reformer 2. Liquor processing in Reformer 2 was reduced to a bare minimum until Reformer 1 reached full operating temperature. After Reformer 1 reached full temperature, liquor processing was increased on both units. Due to the higher amount of fluidizing steam flow through the superheater, the steam temperature was always below target causing an increase in tar formation compared to the one reformer operation. Both units operated on liquor for approximately 8 days at liquor processing rates between 60% and 80% of plant design. On August 30, Reformer 2 tripped due to tars plugging the venturi scrubber and the unit was taken down for an extended outage.

Run 15 continued on Reformer 1 until October 10. The operation was suspended due to tar plugging the Gas Cooler demisters. Several attempts were made to clean the demisters with the reformer in operation, but these were not successful. During Run 15, Reformer 1 operated at the liquor design rate for the majority of the time. The percentage of black liquor converted to tar increased at the higher liquor processing rates which increased the pluggage problem in the gas clean up system. The data from this run will be compiled and analyzed during the next period.

### **Report 40850R20 for the period from 10/2/05 through 12/31/05**

Although run 15 continued on Reformer 1 until October 10, this run was reported in the last report. The cause of the termination of run 15 was tar accumulation and plugging in the gas clean up system. The majority of the time during this period was spent on cleaning out the gas clean up system and inspecting all of the equipment. Several changes were implemented in the gas clean up system to reduce the plugging problem. Spare pumps and piping were added to the venturi scrubbers. These pumps were equipped with strainers identical to the units used on the original pumps. All of the new piping as well as all of the strainers were insulated to prevent heat loss which allows the tars to build up on the colder surfaces. The part of the venturi scrubbers which was not previously insulated, was insulated during this period. The piping to the venturi throat was modified to allow for cleaning and unplugging while still in operation. A system was installed to allow for the feed of a chemical dispersant to both the venturi scrubbers

and the gas cooler circulation loops. All of these changes were designed to prevent the accumulation and deposition of tars in the equipment and piping.

The liquor injectors were modified to a 'flat spray' design to determine if this would improve carbon conversion and reduce the formation of tars. This design of injectors is not steam atomized, but more of a flat fan spray caused by the spray tip. The liquor is still mixed with steam in the injector barrel, but is not atomized. Thermocouples were installed in the injection zone (area between the top of the fluidization grid and the bottom of the lowest pulse heater) to measure the bed temperature in this zone. It is believed that liquor injection is reducing the temperature in this zone. The slow heat up of the liquor may lead to increased formation of tars. The flat spray injection pattern should allow better contact with bed solids and minimize any plumes from the injectors that may heat up at a slower rate. A feasibility study was conducted to determine if a fired superheater for the fluidizing steam would reduce the tar formation. It was determined that additional information was required. The data collected from the injection zone thermocouples and additional trials on the PDU at the University of Utah will be used to complete the study.

The AZ-10 refractory previously installed in the pulse heater combustion chambers did not hold up as expected. The AZ-10 material on all of the pulse heaters of Reformer 1 was replaced with Express 30. The gunnite material used for the water jacket refractory also failed. This material was replaced with Kast-O-Lite 30LIG as a trial. The new refractory will be evaluated after approximately one month of operation before any changes are made to Reformer 2. All of the pulse heater exhaust ducts were inspected for damage. Temporary repairs were again made to the ducts on Reformer 1, while replacement ducts designed without the internal refractory lining were being fabricated for both units. All of the elbow sections will be replaced with the new design during the next periods. It is possible a stainless steel liner will be required to hold the refractory lining in place for the vertical runs.

Run 16 started on 12/16/05 with liquor injection beginning 12/18/05. The new aerovalve design was to be installed in the unit, but was not available in time. The aerovalve will be installed during the next period for evaluation. Since the new assembly was not available, GP designed and implemented temporary weld repairs to all of the aerovalves on two of the original assemblies that had indications of cracking due to overheat. These repairs will also be evaluated during the next period. On all aerovalves of Reformer 1, every other gas jet was plugged to increase the fuel pressure drop across the valves. This is intended to eliminate possible fuel distribution problems.

The individual flow meters installed in two of the liquor injectors were evaluated. These were determined to provide an accurate indication of the liquor flow to the injector. Next period, meters will be acquired for the remaining injectors and installed during outages.

Installation of the HRSG 1 sootblower system was started during this period, but was not completed. All of the internal work was completed, so the unit can be commissioned and placed in service next period while the reformer is in service.

At the end of run 12 on Reformer 2, the internal inspection revealed damage to pulse heater PH2-4. This damage was caused by the violent action of the bed in the upper regions. The unit at Norampac has experienced similar damage. [This statement is not intended to imply the cause or extent of damage in the Norampac unit was the same as in the GP unit.<sup>2</sup>] The mid-baffle of the unit was ripped loose from the 6 support rods. The support rods were also ripped loose from the pulse heater tube sheet and were found at the bottom of the unit. All of the tube surface thermowells were also ripped loose and found in the bottom of the unit. This pulse heater was modified to eliminate the mid-baffle support rods and thermowells. An additional dummy tube with thermocouples was added to the top row of tubes to identify if the bed level ever drops below the top of the heater during operation. Control of the heater in the future will be based on the temperature readings from the dummy tubes.

The pulse heater which was retubed the previous period has been installed in the PH2-1 position. This unit includes the full length test tubes of various metallurgies. This unit will be placed in service next period.

During this period several engineering studies were conducted. It has been determined that a dry bed removal system will be required for long term operation of the system. During each outage, a small portion of the bed is lost and can not be replaced. It is very difficult to operate the reformer with less than a full bed, so building bed level after start up is not practical. A project to design and install a dry bed removal system will be proposed for funding next period. Current operation has been proven to be cooling tower capacity limited. The process is operating with excess fluidization steam due to not being able to place the recycle gas eductor in service. This has increased cooling load on the gas cooler and has resulted in an increased load to the cooling tower. A project to increase cooling tower capacity will be developed next period. An engineering study was conducted to determine if the green liquor filter could be modified to improve the throughput with the high load caused by the poor reformer carbon conversion. Filter bags of a new design were installed, but the improvement was marginal. It was determined that additional equipment would be required to resolve the problem. A project scope will be prepared during the next period.

Since the number one problem impacting the operability of the system is the accumulation of tar in the gas clean up system, several options to address this problem are being considered. In addition to the changes to the gas clean up system described above, GP began an engineering study with several suppliers to investigate options for converting the tars to useful products or fuels. During the next period, additional testing and work with researchers will be conducted to acquire data required by the suppliers to refine alternatives. The goal of the engineering study will be to develop a biorefinery or biofuels solution to the tars in the gas clean up system.

#### **Report 40850R21 for the period from 1/1/06 through 3/31/06**

As reported last period, run 16 started 12/16/05 with liquor injection beginning 12/18/05. During this run, the individual flow meters for the liquor injectors and the weld repair procedure for the aerovalves were proven successful. It was also determined that reducing the number of gas jets on the aerovalves by plugging 50% of the jets improved the performance of the units. The

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<sup>2</sup> Comments to the quarterly report were added during the preparation of the final technical report 1/12/07.

HRSG sootblower system was installed, but not commissioned during this run. Liquor injectors Rev. 4 were fitted with a Bete size 40 flat spray tip. This tip size was determined to be too large and had to be throttled with manual valves. Due to the refractory failures in the combustion chamber, all of the refractory in the Reformer 1 pulse heater combustion chambers was replaced with Harbison-Walker Express 30 material for evaluation. Also, in an effort to reduce the tar plugging of the gas clean up system, a chemical dispersant was tested. The trial demonstrated this chemical is effective in preventing the deposition of tars on the wetted surfaces.

At the end of run 16 a very short outage for the inspection of the pulse heater combustion chamber refractory was conducted. We attempted to conduct the inspection without removing the bed media from the vessel. In order to accomplish this, the bed was kept fluidized with air while the inspection was conducted. We attempted to install the new design of aerovalve during this outage, but were unable to fit the unit in place due to the vessel movement caused by the fluidization. After the inspection, warm up for run 17 was started on 1/25/06. During the warm up period, fluidization air was temporarily lost to the vessel allowing the bed to slump. Bed was again fluidized after 2 hours. Liquor injection was started the evening of 1/27/06, but was discontinued after 10 hours due to high dummy tube temperatures in the bottom 2 pulse heaters. It appears that after the bed slumped during warm-up; the material within these pulse heaters was not sufficiently fluidized to allow operation.

After run 17, several modifications were made to Reformer 1. Inspection of the refractory in the pulse heater combustion chambers revealed the Express 30 material had failed in 3 of the pulse heaters. Analysis of the failed material indicated the material had been exposed to combustion chamber temperatures in the range of 2800 ° to 3200 °F. The temperature measured by the thermocouples embedded in the outer ring refractory in the pulse heater generally ranges between 2200 ° to 2400 °F. An extended thermocouple was installed in one of the units to determine if there was a measurement system error. The refractory in the 3 units was replaced with various materials to determine if one type would hold up better than the others. The materials tested were Harbison-Walker Ultra Express 70, Harbison-Walker Greencast 94 Plus, and Resco EZ Cubed 60M. The injectors were also fitted with Bete size 20 flat spray nozzles. Warm-up for liquor run 18 started on 2/21/06 and liquor injection started on 2/23/06. The liquor run was terminated on 2/26/06 due to problems with the liquor injection system.

After run 18, the system was shut down and inspected. It was determined that the liquor system problems were a combination of faulty heat tracing of liquor lines and the smaller injector tips. The pressure drop across the smaller tips was too high for the existing liquor pumping and heating system. Also several of the injector tips had failed due to differential expansion between the liquor barrel and the annulus pipe. The liquor injectors were modified to revision 5 designed to eliminate the differential expansion problem. Bete size 30 flat spray nozzles were installed on the injectors. Inspection of the refractory did not find any issues after the short run. Warm up for liquor run 19 started on 3/9/06 and liquor injection started on 3/12/06. The liquor run was terminated for a scheduled inspection of the pulse heater refractory on 4/7/06. Inspection of the refractory indicated the Harbison-Walker Greencast 94 Plus is the best choice for installation in the units of Reformer 2. The other refractory materials remained in serviceable condition and will not be replaced prior to the next run of Reformer 1. The modified liquor injector design was

successful in eliminating the differential thermal expansion failures. The liquor injection was stable and well controlled during this run.

#### **Report 40850R22 for the period from 4/1/06 through 6/30/06**

Liquor run 20 on Reformer 2 was started on 4/30/06 with liquor injection on 5/02/06. This run was still in progress at the end of the period. During this run, several failures of the fabric expansion joints on the pulse heater exhaust ducts were experienced. As previously reported, sections of this duct between the reformer and the expansion joints were replaced with stainless steel duct due to the failure of the internal lining of the original duct. The design of the duct by the supplier did not properly account for the new thermal expansion of the stainless duct. The increased thermal expansion of the stainless duct caused a displacement in the expansion joints which eventually led to failures. Also during this run, failures of the internal lining of the vertical sections of this duct were discovered. Temporary repairs were implemented to the expansion joints and fans were used to cool the vertical sections. The design of replacement ducts and expansion joints was completed.

Liquor run 21 on Reformer 1 was started on 5/15/06 with liquor injection on 5/17/06. This run was terminated on 6/26/06 as part of the mill's flood preparation plan. Due to the length of time required to cool the bed and remove it to the Media Storage Silo, the shut down decisions for the reformers occur very early in the flood preparation plan. Shutdown of Reformer 2 was also scheduled to follow, but the prediction for the river crest was lowered and the unit was kept on line. During this run, Reformer 1 also experienced failures of the pulse heater expansion joints and vertical duct. After run 21, 4 water leaks were discovered in the tube sheet of PH1-1. These leaks were weld repaired and the tubes were plugged. Also, a crack in the weld between the reformer vessel and the PH1-2 Decoupler was discovered. This crack allowed bed solids to be blown from the reformer to the exhaust duct of the pulse heater. Inspection of the other units revealed similar cracks. All of these were weld repaired.

During the period when both reformers were in service, the heat load on the Cooling Tower was above the operating capabilities of the tower. Modifications made to the cooling system in an attempt to allow operation of both units at full load were not successful. On 6/12/06, a rental cooling tower was placed in service to eliminate this problem. Engineering data continued to be collected at the end of the period to better size a replacement tower.

For the shutdown of run 19, the project team successfully used water injection to cool the reformer bed. For the start up of run 21, the project team successfully started the unit up with only 3 pulse heaters covered with bed solids. Liquor injection was used to increase the bed level to the normal operating level before PH1-4 was placed on main flame. By accomplishing both of these items, the scope of the Dry Bed Removal system will be significantly reduced.

#### **Report 40850R23 for the period from 7/1/06 through 9/30/06**

Liquor run 20 on Reformer 2 was started on 4/30/06 with liquor injection on 5/02/06. This run was terminated on 7/12/06 due to problems with the gas clean up system. Tar formation in the gas clean up system led to plugging of the Gas Cooler Heat Exchangers. Attempts to clean the

tar from the system on the run were not successful. During this period, the Reformer Boiler tripped off line due to the extremely high moisture content of the wet fuel from the Gas Cooler. This was a result of the tar fouling of the Gas Cooler Heat Exchangers and led to slumping of the Reformer 2 bed due to loss of fluidization steam. It was decided to take the unit down after the third slump in 2 days. During the outage, tube sheet cracking was found in PH 2-1 and PH 2-2. Three leaks were repaired on PH 2-1 and two leaks were repaired on PH 2-2. All leaks were repaired by welding and the tubes impacted by the leaks were returned to service.

Liquor run 22 on Reformer 1 started 7/5/06 with liquor injection starting 7/7/06. As soon as liquor injection on Reformer 1 started, the Gas Cooler exhaust temperature became a problem indicating the heat exchangers were fouled to the point they could not handle the additional load. As liquor load was increased, the wet fuel temperature leaving the Gas Cooler increased to the point the Reformer Boiler tripped off line. The steam header swing caused by the trip resulted in a slumped bed for Reformer 2. During this run, the expansion joint on the exhaust of PH 1-2 failed requiring the pulse heater group to be shut down to allow for temporary repairs. Due to the leaks found in the units of Reformer 2, liquor run 22 was terminated on 7/27/06 to inspect the pulse heaters. During this outage, work common to both reformers was performed. This included inspection and cleaning of the Gas Cooler and Gas Cooler Heat Exchangers, Reformer Boiler inspection and removal of tar from both venturi scrubbers and piping.

After completion of the outage work, liquor run 23 on Reformer 2 started on 8/5/06 with liquor injection beginning 8/7/06. Smaller injectors were installed as a trial on this liquor run. This was followed by liquor run 24 on Reformer 1 on 8/7/06 with liquor injection on 8/9/06. The staggered start was required because the fluidization air compressor has the capacity to start only one reformer at a time. After several days, the bed particle size for Reformer 2 indicated the mean particle size was decreasing, probably due to the smaller liquor injectors. On 8/13/06, PH 1-2 was taken off main flame due to suspected bed side plugging. Beginning 8/21/06, operations experienced high temperature alarms on the PH exhausts of PH 2-1 and PH 2-2. In spite of these alarms, the operators were not able to maintain bed temperature without reducing the liquor throughput. Liquor run 23 was terminated on 8/23/06 due to leaks in the PH 2-2 tube sheet. After several days, the bed particle size for Reformer 2 indicated the mean particle size was decreasing, but due to the limited length of the trial, the final particle size did not reach a stable value. On 8/24/06, PH 1-3 began to show signs of bed side plugging. Since PH 1-2 was already down, liquor run 24 was terminated on 8/25/06. Subsequent internal inspection of Reformer 1 confirmed both heaters were plugged.

On 8/21/06, members of the project team participated in a meeting in Montreal, Canada with Norampac, TRI, and BodyCote (metallurgical lab investigating the Norampac PH tube sheet cracking) to review the recent failures of both Norampac and GP pulse heaters. [During the meeting it was determined that the cause of cracking in the GP combustion chamber tube sheets was different than at Norampac.<sup>3</sup>] Based on the information exchanged at this meeting, GP inspected the exhaust end of the pulse heaters for bowing of the exhaust tube sheet. Three pulse heaters were observed to have exhaust tube sheets which were bowed approximately 0.75" with the center section of the tube sheet deflected towards the exhaust. Other heaters were not measured, but appear to have a similar issue.

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<sup>3</sup> Comments to the quarterly report were added during the preparation of the final technical report 1/12/07.

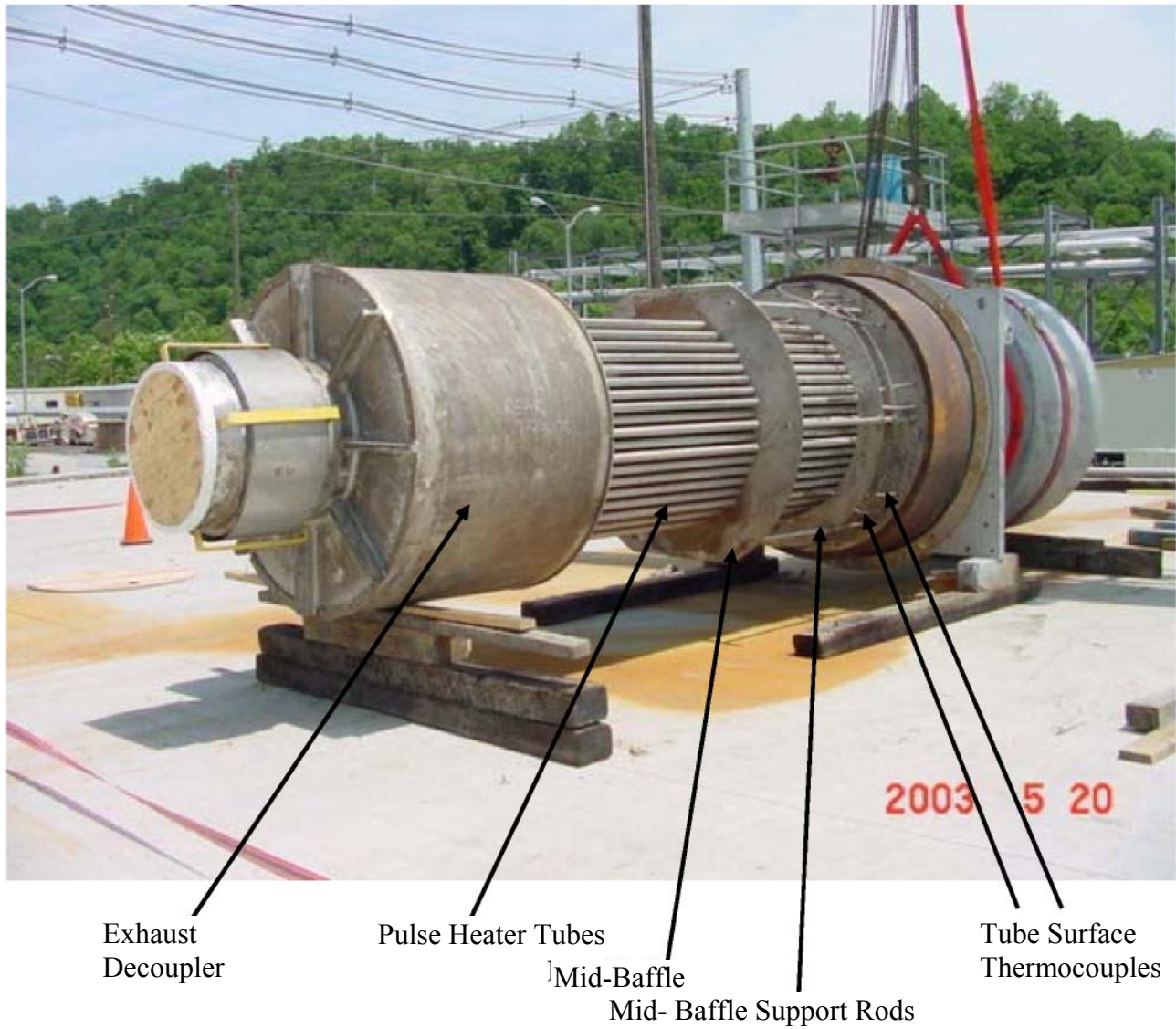


Problems identified during the inspection of the reformers included:

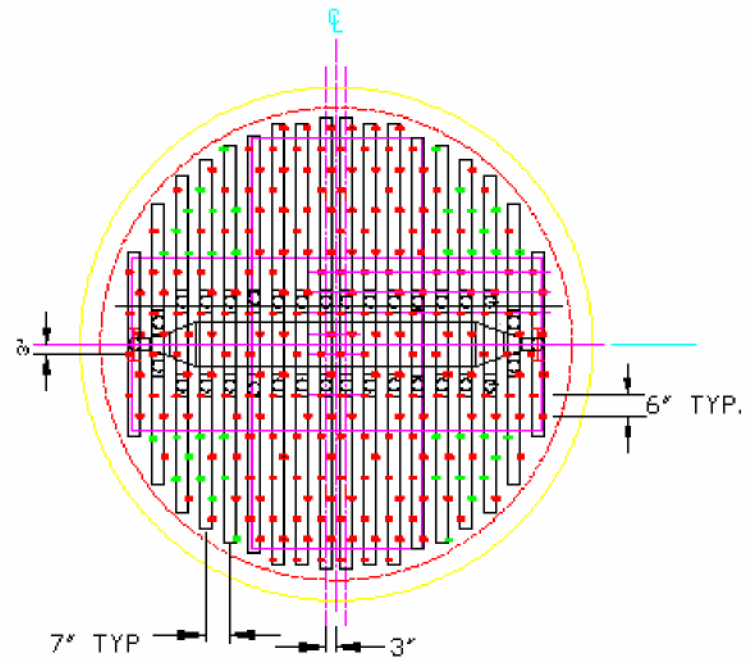
- 26 tube sheet leaks in PH 2-2 plus an unidentified number of leaks on the bed side tube sheet. Due to the design of the pulse heaters, detailed inspection of the bed side tube sheet is not practical.
- Significant number of tube failures in PH 1-2 due to overheat when the tube bundle partially plugged with bed solids.
- Aerovalve assemblies (original design which were weld repaired) for PH 1-2 and PH 1-3 had cracks at the aerovalve tips. This could possibly have led uneven heat distribution in the combustion chamber and plugging of the heater bundles.
- Bowing of the exhaust end tube sheets.
- Cracking and tube failures at the exhaust end tube sheets possibly due to localized overheating.
- Bowing of the outside tubes of the pulse heater tube bundles.

## Appendix 5

### Pulse Heater

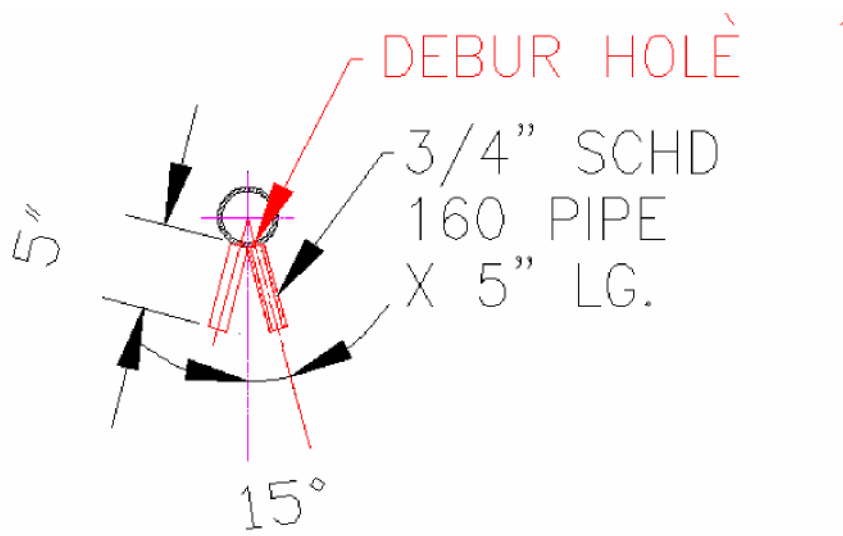


## Appendix 6 Fluidizing Grid



**GRID GP-4**

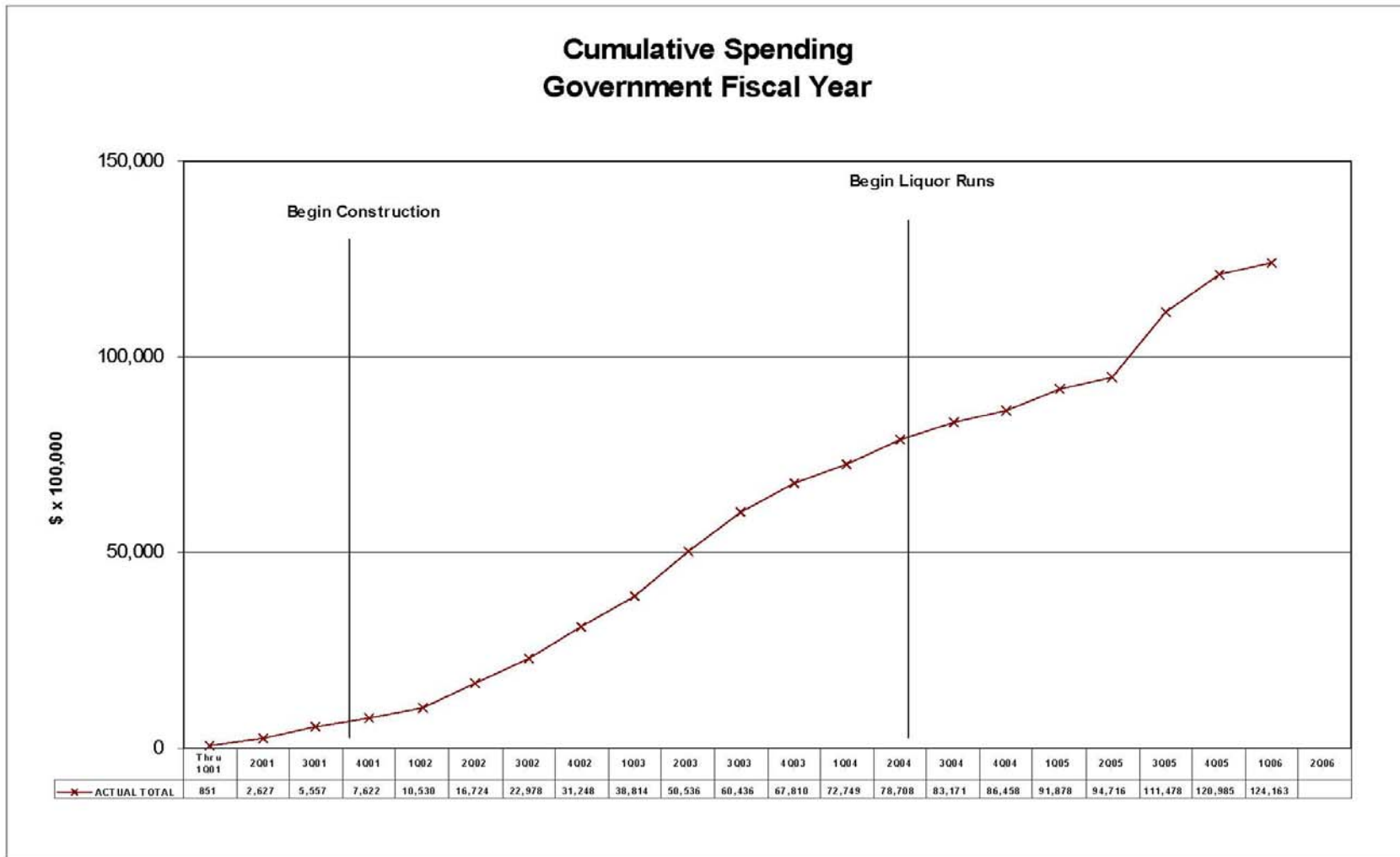
Nozzle Locations



Nozzle Design

## Appendix 7 Cost Information

Cost information from Quarterly Report 40850R23 – period ending 9/30/06.



Cost information from Quarterly Report 40850R23 – period ending 9/30/06.

| Project Budget Period | Period       |              |               | Cumulative   |              |               |
|-----------------------|--------------|--------------|---------------|--------------|--------------|---------------|
|                       | DOE          | G-P          | Total         | DOE          | G-P          | Total         |
| 7/1/06 - 9/30/06      | \$0          | \$ 6,271,758 | \$ 6,271,758  | \$44,239,118 | \$94,466,986 | \$138,706,104 |
| Previous Total        | \$44,239,118 | \$88,195,228 | \$132,434,346 | 31.9%        | 68.1%        | 100.0%        |

Note: Table has been modified to reflect actual payments by DOE. DOE retains \$200,000 pending final report.

| DOE Obligated Funds |              |              |            |
|---------------------|--------------|--------------|------------|
| Amendment           | Amount       | Total        | Date       |
| 000                 | \$4,537,776  | \$4,537,776  | 2/13/2001  |
| 001                 | \$0          | \$4,537,776  | 4/25/2001  |
| 002                 | \$0          | \$4,537,776  | 5/3/2001   |
| 003                 | \$0          | \$4,537,776  | 8/13/2001  |
| 004                 | \$0          | \$4,537,776  | 8/17/2001  |
| 005                 | \$4,671,000  | \$9,208,776  | 9/10/2001  |
| 006                 | \$13,130,000 | \$22,338,776 | 9/17/2001  |
| 007                 | \$162,665    | \$22,501,441 | 9/26/2001  |
| 008                 | \$0          | \$22,501,441 | 10/31/2001 |
| 009                 | \$0          | \$22,501,441 | 11/6/2001  |
| 010                 | \$6,385,000  | \$28,886,441 | 2/1/2002   |
| 011                 | \$3,684,000  | \$32,570,441 | 9/16/2002  |
| 012                 | \$44,540     | \$32,614,981 | 9/30/2002  |
| 013                 | \$4,000,000  | \$36,614,981 | 3/24/2003  |
| 014                 | \$4,408,000  | \$41,022,981 | 5/7/2003   |
| 015                 | \$3,000,000  | \$44,022,981 | 4/5/2004   |
| 016                 | \$416,141    | \$44,439,122 | 5/11/2004  |
| 017                 | \$0          | \$44,439,122 | 5/27/2004  |
| 018                 | \$0          | \$44,439,122 | 7/26/2004  |
| 019                 | \$0          | \$44,439,122 | 10/20/2004 |
| 020                 | \$0          | \$44,439,122 | 3/28/2005  |

## **Appendix 8 (Supplied by DOE)**

### **Summary of Steam Reformer Safety, Operational and Maintenance Experience and Achievements at Norampac**

#### **Introduction**

TRI licensed its technology for a black liquor steam reformer to Norampac in about 2000 the same time it licensed a similar project to Georgia-Pacific in Virginia. The Norampac steam reformer started up first and achieved some different operational results. Following is a summary of the project, the Norampac achievements and a discussion of some of the significant design differences.

#### **Background**

Norampac recently became a wholly owned subsidiary of Cascades and is Canada's largest containerboard manufacturer. The Norampac Trenton mill in Ontario, Canada, is located on the Trent River, a popular recreation area. The mill, which has been a zero effluent mill since 1996, produces 500 mtpd of corrugating medium. Prior to the start-up of the TRI steam reformer the mill had no chemical recovery system. For over forty years the mill's spent liquor was sold to local counties for use as a binder and dust suppressant on gravel roads. This practice was discontinued in 2002 with the utilization of TRI's steam reformer technology to recover pulping chemicals and energy from its black liquor.

The original design capacity of the TRI spent liquor gasification system was 115 mtpd (126.7 short tons /day) of black liquor solids (BLS), a little more than half the capacity of the Virginia project. This capacity was substantially more than needed to support pulping operations, but provided the flexibility to dispose of stored liquor in the short term and provide capacity for pulping capacity increases in the long term. Norampac utilized one reformer vessel with 4 pulse heaters, whereas the Virginia project utilized two reformer vessels with 4 pulse heaters each. At Norampac, the syngas was cleaned of particulates and burned in a down fired Foster Wheeler boiler. Since the mill's only power boiler operated on natural gas, the pulse heaters were fired on natural gas, so no gas cleanup was required. Subsequent to startup, the plant was re-rated to 85 TPD BLS (67% of original design) with the ability to achieve that capacity with just three pulse heaters. The plant was permitted at the new capacity.

TRI's scope of supply included the steam reformer, pulse combustors and fuel train, materials handling equipment, instrumentation, detailed engineering, operator training and start-up support.

The process started up in September of 2003.

The project completed its performance test in April of 2005 and it completed air emissions testing in October 2006 thereby transitioning from commissioning to full commercial operation. Norampac and TRI are collaborating to continue system optimization.

## **Project Achievements**

During project execution, construction commissioning and continuous operation, the reformer system has proven to be safe and reliable, with no lost time accidents or incidents recorded.

The system demonstrated 91.5% availability in 2005 and 87.2% in 2006 out of a budgeted 330 day operating year. To date the system has accumulated over 18,000 hours of operation while recovering 97.5% of the sodium in the liquor.

The system produces steam for export to the mill even though carbon conversion is below target. The companies have formed a user's group to continue improvement of reformer performance and there are two areas of carbon conversion improvement being actively developed and tested.

Following successful commissioning and operation, the stability of the system has allowed Norampac to reduce staff to only one operator per shift and his duties include sample testing. The system is supported by a process engineer who also handles other mill duties.

## **Optimization Efforts and Results**

Norampac, Georgia-Pacific and TRI collaborated through a joint working group to optimize the major common issues of carbon conversion and pulse heater reliability. However, in addition to the common issues, the larger capacity unit also faced a number of other challenges, including fluidization uniformity, exhaust duct failures, heater refractory life, cyclone carryover, bed drain, tars generation, etc. The Virginia unit and the Norampac systems differed, not only in the two core areas needing improvement, but also in other areas that were not common to Norampac, that being the area of liquor distribution across the cross section of the reformer and removal of bed material from the bottom. As part of its licensor responsibilities TRI issued process performance specifications to both clients that specified a number of important process parameters. At Norampac, TRI was responsible for the design of the reformer system and as a result, these specifications were followed by the engineering consultant. During design and construction, TRI and Norampac collaborated in every detail.

**Reformer Fluidization** –Norampac experienced a smooth initial start-up. The reformer island was mechanically completed in June 2003 and pre-commissioning activities were finalized in July 2003. Process commissioning commenced in August 2003, with several short campaign runs, during which the steam distribution grid and injector tips were modified to optimize performance.

The first sustained steam reformer run took place from October – December 2003. The reformer island achieved 100% availability and design capacity, and processed all the black liquor produced by the pulp mill during that period, returning consistent quality cooking liquor back to the mill. This was an outstanding accomplishment for a “first of the kind” commercial installation of new technology.

The GP steam reformers operated at up to 70% of design capacity for periods of 10 to 75 days duration. One startup problem experienced on one of the steam reformers was bed agglomerations inside the heater bundles necessitating a shutdown of the system. By undertaking 1/3 scale cold flow modeling of the reformer system using both the steam grid

designs, it was confirmed that the non-uniform bubble cap pattern in the one grid configuration was causing non uniform fluidization, resulting in bed agglomeration in the heater bundle. Further cold flow trials resulted in a steam grid design that allowed for a step change in reformer performance. Utilizing the results from both cold flow modeling and full scale testing at the Virginia unit, TRI has designed a second generation steam grid, which TRI believes will surpass the performance of the Norampac bubble caps. Norampac is still operating with the original steam grid, but is considering the installation of the new design in a future outage. The new design improves fluidizing steam distribution and TRI expects to achieve better steam/particle contact and hence an increase in carbon conversion.

**Fluidizing Steam Temperature** – The fluidizing steam temperature is superheated through heat recovery with the PC heater flue gas. At Norampac, the fluidizing steam is superheated to 1100 °F, but at the unit in Virginia the fluidizing steam was delivered at approximately 900 °F. The zone between the steam grid and the liquor injector, where the steam partial pressure is high, represents the char reaction zone. When steam is introduced below its reaction temperature, the efficiency of char conversion could be decreased. Attempts were made to try to measure the temperature impact above the grid; however, because of the very high heat transfer between the bed solids and the temperature probe, the effect is very difficult to measure. Any energy extracted from the bed material to heat the fluidizing medium up to bed operating temperature robs energy from the injection zone, which has a very high energy demand. Colder injection zones can lead to higher tar formation during pyrolysis of the liquor. This situation possibly could be addressed by the installation of a duct heater or secondary superheater system to increase the fluidizing medium temperature.

**Liquor Uniformity** – TRI specified for Norampac uniform liquor injection utilizing the complete cross-section of the reformer to maximize liquor contact with the fluidized bed. TRI feels this promotes rapid heating of the liquor by the bed solids which maximizes volatile yield and minimizes tar production. In addition, since the black liquor feeds to this unit contains 40% water, the resulting steam bubbles would then be uniformly distributed over the bed cross section for consistent fluidization. For this liquor, the target injection flow is about 1 GPM/injector and Norampac had 28 liquor injectors that penetrated the bottom of the vessel in a uniform pattern. During operation, the introduction of liquor in this distributed manner is believed to contribute to the uniformity of bed fluidization. The Virginia units had 12 liquor injectors that penetrated the side of the vessel forming a circular pattern. In addition, due to layout constraints, the liquor injectors were positioned such that only 3 of the 12 injectors were below the criss-cross heater bundles, with the balance pointing directly into the open quadrants. The high liquor flow per injector and the injector layout may have resulted in bypassing of the heater bundles, resulting in cooler liquor injection zones, more tars production and reduced carbon conversion. Recently injector tests at the pilot scale at the University of Utah are attempting to show the impact that well atomized liquor droplets that are uniformly distributed over the whole bed cross-section have on syngas generation and carbon conversion. The results of these tests will be reported upon completion of the work.

Heat transferred measured in the PC heater tube bundles at Norampac was excellent, and the overall heat transfer coefficients were at 95% of maximum design coefficients. The GP unit utilized steam diluted natural gas firing of the PC heater and this could have contributed to a



lower overall heat transfer coefficient. Lower heat transfer coefficients could also result from higher liquor flows per injector (larger steam bubbles at injectors) and a less distributed injection pattern could cause disruptions in bed fluidization and encouraged heater bypassing. The result could be sub-optimal fluidization inside the heater bundles, inhibiting heat transfer performance.

TRI continues to design and test improved injector configurations with the goal of maximizing injection uniformity and control. Norampac has had sustained runs with the new design in some of the injector positions and based on the observed improvements, is in the process of converting the remaining injectors.

**Bed Removal** – Norampac has had relatively good experience with the TRI-specified removal of the bed from the bottom of the vessel through three lock hoppers. Note that bed material extracted from the reformer bottom has passed through the char conversion zone. On the Virginia unit, the bed material is removed from the side of the vessel via a single lock hopper, near the first pulse heater, and directly above the liquor injection zone. Extracting bed material at this point could change bed material flow patterns in the vessel, and under certain part-load conditions. Temperature cycles observed in the PC Heater dummy tube temperatures corresponded to the cycling of the lock hopper, indicating that this lock hopper cycling could have aggravated the uniformity of fluidization. Over an extended period of operation, the possibility exists that larger particles would accumulate at the bottom of the reformer. When these larger particles built up to the level above the steam grid, the bed fluidization would likely be compromised. The installation of a manual intermittent single lock hopper system at the bottom of the reformer was made to address this concern. However, the samples of material taken from the GP single lock hopper system did not show a difference in particle size between bottom and side withdrawal.

**Pulse Heater Reliability** – Full scale operation of the PC heaters in all units have revealed that there were several areas that needed design improvement: aerovalve assemblies, temperature measurement, baffles and the decoupler seal. In an inspection at Norampac immediately after the first sustained long operation, serious damage was found on the aerovalves, which control the pulse combustion process. Forensic metallurgical tests were conducted in Canada and USA to determine the cause. The operating temperature of these aerovalves was substantially above those predicted in the FEA design models. The aerovalves were rebuilt for Norampac using upgraded metallurgy but TRI/Norampac continued engineering of an improved design. Our collaboration through the user group resulted in the next generation aerovalve assembly that was fabricated and tested on the Virginia unit with encouraging results.

The original pulse heater design incorporated thermocouples on the outer tubes to control heater firing and indicate overheating of the tubes. During startup, especially with the initial limestone bed, the tube bundles were subjected to large structural loads and the thermocouple support rings and baffle design proved inadequate. As a result some of the thermocouples were lost. In addition, it was possible to have undetected hot spots in the center of the bundle that the outer thermocouples could not detect. Working in collaboration with the users group, the tube bundle has been redesigned to improve structural rigidity and distribute thermocouples in the interior of the bundle. This new configuration has been fabricated and is being tested at Norampac.

All units contain pulse combustor heaters that demonstrated a bowing of the decoupler tube sheet and subsequent misalignment of outer tubes. Forensic examination has determined that the bowing is caused by the binding of the decoupler in the exhaust nozzle. Thermal expansion and contraction of the tube bundle then stresses the tube sheet causing it to bow. The existing packing schemes are inadequate and we have developed an improved sealing concept that will protect the area between the decoupler and the nozzle. This new design is being finalized and will be tested at Norampac in the near future.

The PC heater refractory at Norampac has continued to perform well over the past three years of operation. The refractory expert engaged to design the refractory system stressed that the selection of the refractory was only part of the solution; to obtain good performance of the refractory system the correct installation procedure was key. After testing several different refractory materials, it was concluded that refractory can be over heated because of maldistribution of combustion air, resulting from the air intake being much smaller than recommended. By designing and installing a distributor to improve combustion air distribution to the aerovalves, the combustion chamber temperatures cooled and became more uniform resulting in dramatically improved refractory life.

TRI has undertaken a redesign of the interior combustion chamber tube sheet to ensure robust performance and sustain the tube sheet in the case of boiler feed-water failures. This modification along with the changes to the tube bundle design and decoupler seal improvements should prevent any further issues with the combustion tube sheet integrity.

## **Summary**

Black liquor steam reformer technology at Norampac has been a success. TRI's partnership with Norampac will result in continued improvement of the technology.